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TITLE:

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Aq. dispersion contg. polymer for glazing of

floors -

consisting of compsn. including glycidyl

methacrylate,

methacrylic acid, styrene and ethyl acrylate

PATENT-ASSIGNEE: LION CORP[LIOY]

PRIORITY-DATA: 1993JP-0332631 (December 27, 1993)

PATENT-FAMILY:

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ABSTRACTED-PUB-NO: JP 07188345A

**BASIC-ABSTRACT:** 

An aqueous dispersion containing polymer is one in which a copolymer from the

monomers (1), (2), (3), and (4) specified below is dispersed in an aq. medium:

(1) 1-20 wt. % an ethylenically unsaturated monomer having an oxirane group,

represented by the formula (I), (2) 7-23 wt. % an alpha, betaethylenically

unsaturated carboxylic acid, (3) 5-55 wt. % an aromatic vinyl monomer, and (4)

15-87 wt. % acrylic and/or methacrylic esters. R1 = H or CH3; X = -0-,

-C(0)-O-R2, or -CH2-O-; R2 = 1-10 C alkylene.

USE - This aq. dispersion is used for an aq. glazing agent for floors, furniture, etc. ADVANTAGE - This glazing agent gives to floors and furniture not only lustre but also resistance to water, chemicals, and heel mark. CHOSEN-DRAWING: Dwg.0/0 TITLE-TERMS: AQUEOUS DISPERSE CONTAIN POLYMER GLAZE FLOOR CONSIST COMPOSITION GLYCIDYL METHACRYLATE METHACRYLIC ACID STYRENE ETHYL ACRYLATE DERWENT-CLASS: A14 A82 G02 CPI-CODES: A04-C01A; A04-F01A1; A05-A04; A07-B02; A07-B03; A12-B01A; G02-C; ENHANCED-POLYMER-INDEXING: Polymer Index [1.1] 017 ; G0022\*R D01 D51 D53 D12 D10 D23 D22 D31 D42 D58 D63 D84 D85 D86 D87 D88 D89 D90 D91 D92 D93 D94 D95 F34 F41 F47 ; G0022\*R D01 D51 D53 D60 F35\*R; G0102\*R G0022 D01 D12 D10 D18 D51 D53; G0340\*R G0339 G0260 G0022 D01 D12 D10 D51 D53 D58 D63 F41 G0384\*R; P0464\*R D01 D22 D42 F47 ; H0033 H0011 ; S9999 S1025 S1014 ; P1741 ; P0088 Polymer Index [1.2] 017 ; ND01 ; Q9999 Q7114\*R ; Q9999 Q7181 Q7114 ; Q9999 Q6848 ; Q9999 Q7716 Q7681 ; B9999 B4411 B4400 B4240 ; B9999 B4706\*R B4568 ; B9999 B4580 B4568 ; K9483\*R ; K9676\*R ; K9712 K9676 ; ND04 Polymer Index [2.1] 017 ; R00460 G0306 G0271 G0260 G0022 D01 D12 D10 D51 D53 D58 D60 D84 F36 F35 ; R00708 G0102 G0022 D01 D02 D12 D10 D19 D18 D31 D51 D53 D58 D88 ; R00800 G0384 G0339 G0260 G0022 D01 D11 D10 D12 D23 D22 D31 D42 D51 D53 D58 D63 D87 F47 F41 ; R01126 G0340 G0339 G0260 G0022 D01 D11 D10 D12 D51 D53 D58 D63 D85 F41 ; R00479 G0384 G0339 G0260 G0022 D01 D11 D10 D12 D51 D53 D58 D63 D85 F41 ; H0033 H0011

017 ; ND01 ; Q9999 Q7114\*R ; Q9999 Q7181 Q7114 ; Q9999 Q6848

; S9999 S1025 S1014 ; P1741 ; P0088

Polymer Index [2.2]

; P0464\*R D01 D22 D42 F47 ; L9999 L2528 L2506 ; L9999 L2551 L2506

Q6826

; Q9999 Q7716 Q7681 ; B9999 B4411 B4400 B4240 ; B9999 B4706\*R B4568

; B9999 B4580 B4568 ; K9483\*R ; K9676\*R ; K9712 K9676 ; ND04 Polymer Index [2.3]

017 ; B9999 B3598 B3554 ; B9999 B3430 B3372

Polymer Index [2.4]

017 ; R03252 D00 F16 F48 F60 H\* N\* 5A O\* 6A S\* ; C999 C088\*R C000 ; C999 C293

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention makes an active principle a polymer content aquosity dispersing element suitable as an active principle of aquosity polish, and this aquosity dispersing element, and relates to the suitable aquosity polish for a floor, furniture, etc. [0002]

[Description of the Prior Art] It is required for the polish used for a floor etc. to carry out glazing generally that beautiful gloss is discovered and maintained, that a black heel mark cannot adhere easily, that leveling nature is good, that removal nature should be good, etc. Conventionally, the aquosity polish which blended alkali fusibility resin, the plasticizer, the wax agent, the surfactant, etc. with the acrylic resin emulsion for the purpose of fine sights, such as a floor and furniture, protection, etc. is known. high endurance in which floors, such as a hospital, are asked for these although the approach (JP,47-15597,A) of constructing a bridge with polyvalent metal ion in the acrylic resin containing a carboxyl group as these polish, the method (JP,57-3850,A) of using the reaction of a carbonyl group and a hydrazine radical, etc. are learned -- alcohol resistance was not able to be fulfilled in detail. Moreover, although the approach (JP,55-110170,A) of making an alkoxysilane radical content monomer a constituent, the approach (JP,60-219274,A) of making a constituent an alkoxysilane radical content monomer and colloidal silica, etc. were proposed, as for these, the lifting had during preservation and the alkoxy group had a problem in stability in hydrolysis and condensation. Furthermore, although the approach (JP,57-31969,A) of making a cross-linking partial saturation monomer a constituent was also proposed, the polish which makes the polymer of a publication an active principle concretely here was not what fills all engine performance, such as alcohol-proof, and gloss, black heel-proof mark nature, with sufficient balance.

[0003]

[Problem(s) to be Solved by the Invention] When it is used as an active principle of aquosity polish, this invention gives chemical resistance to \*\*\*\*, furniture, etc., and aims at offering the polymer content aquosity dispersing element which has the outstanding engine performance, such as glossiness, black heel-proof mark nature, and a water resisting property, further. This invention gives chemical resistance to \*\*\*\*, furniture, etc., and aims at the good thing of the balance which was further excellent in glossiness, black heel-proof mark nature, a water resisting property, etc. for which aquosity glazing is carried out and a constituent is offered again.

[0004]
[Means for Solving the Problem] Although it belonged to the subordinate concept of a polish constituent given in JP.57-31969. A. this invention had the property as polish that the polymer which is not indicated

given in JP,57-31969,A, this invention had the property as polish that the polymer which is not indicated concretely was extremely excellent in this official report, and according to this polymer, it was made based on knowledge that the above-mentioned technical problem is efficiently solvable. That is, the polymer content aquosity dispersing element characterized by this invention coming to distribute the copolymer of the monomer of following the (1) - (4) in an aquosity solvent is offered.

(1) 1 - 20 % of the weight [0005] of oxirane radical content ethylenic unsaturated monomers expressed with the following general formula (I)

[0006] (As for H or CH3, and X, R1 is [-O-, -C(O)-O-R2- or -CH2-O-, and R2] the alkylene groups of carbon numbers 1-10 among a formula.)

(2) 7 - 23 % of the weight aromatic-series [(3)] vinyl monomer 5 of alpha and beta-ethylene nature unsaturated carboxylic acid - 55-% of the weight (4) acrylic ester, and/or 15 - 87 % of the weight of methacrylic acid ester monomers.

The oxirane radical content partial saturation monomer expressed with the general formula (I) used by this invention reacts with the carboxyl group in the polymer brought about from a monomer (2), gives cross-linking \*\*\*\*\*\*, and gives chemical resistance and endurance to a polymer. As such a monomer, glycidyl acrylate, glycidyl methacrylate, the glycidyl allyl compound ether, the glycidyl meta-allyl compound ether, etc. are mentioned. One sort of these partial saturation monomers may be used, or they may be used for two or more sorts, combining. The above-mentioned oxirane radical content partial saturation monomer is 3 - 15% preferably 1 to 20% in a monomer weight ratio among a polymer. The chemical resistance which excelled [% / less than 1 ] in this invention cannot be demonstrated, but if [ than 20% ] more, the powdering phenomenon of the so-called paint film which membrane formation nature falls and does not form a continuation coat will be produced.

[0007] (2) alpha and beta-ethylene nature unsaturated carboxylic acid used by this invention gives the removal nature by alkali while giving chemical resistance and endurance to a polymer according to a reaction with the oxirane radical of a polymer, and bridge formation with polyvalent metal ion. The carbon numbers 3-6alpha of an acrylic acid, methacrylic acid, an itaconic acid, a crotonic acid, a fumaric acid, a maleic acid, aconitic acid, etc. and beta-ethylene nature unsaturated carboxylic acid are mentioned that what is necessary is just a monomer containing one or more carboxyl groups. They are the acrylic acid of carbon numbers 3-5, methacrylic acid, an itaconic acid, etc. preferably. Above alpha and beta-ethylene nature unsaturated carboxylic acid are 9 - 19% preferably 7 to 23% among a polymer. At less than 7%, the removal nature by alkali becomes poor, and if [ than 15% ] more, powdering and a waterproof fall will be caused. what gives the gloss excellent in the coat by the high crystallinity whose (3) aromatic-series vinyl monomer used by this invention is the physical property -- it is -- for example, the carbon numbers 8-16, such as styrene, methyl styrene, and vinyltoluene, -- the aromatic series vinyl compound of carbon numbers 8-12 is mentioned preferably. An aromatic series vinyl monomer is 10 - 50% preferably 5 to 55% among a polymer. If gloss sufficient at less than 5% is not shown and 55% is exceeded, a black heel-proof mark and a shock-proof fall will be caused.

[0008] As the acrylic ester used by this invention, and/or methacrylic acid ester, the carbon number of alkyl groups, such as the acrylic-acid alkyl ester of 1-12, a methylmetaacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, and hexyl methacrylate, is mentioned [ the methacrylic acid alkyl ester of 1-12 etc. ] for the carbon number of alkyl groups, such as methyl acrylate, ethyl acrylate, propylacrylate, butyl acrylate, 2-ethylhexyl acrylate, and octyl acrylate, for example. If the carbon number of the alkyl group in these ester exceeds 5, resistance to contamination will fall, if a carbon number approaches 1, a fine residual monomer will release a remarkable offensive odor, and it is not desirable on an activity. It is desirable to use two or more sorts combining the methyl acrylate whose carbon numbers of an alkyl group are 1-4, ethyl acrylate, propylacrylate, n-butyl acrylate, etc. The amount of acrylic ester and/or methacrylic acid ester is 25 - 75% preferably 15 to 87% in a monomer weight ratio among a polymer. In addition, it is good 10 / 90 - 80/20 (weight ratio), and to use acrylic ester and methacrylic ester together so that it may be most preferably set to 30 / 70 - 70/30 especially preferably. The polymer of this invention is a polymer which has the specific monomer presentation ratio of above-mentioned monomer (1) - (4). As for this polymer, it is desirable to have 313-373-degree

K Tg with the glass transition temperature (following for it to abbreviate to Tg) called for from a Fox style usually shown below. For especially discovering the effectiveness of this invention further, 323-363 degrees K is desirable. If lower than this, black heel-proof mark nature will fall remarkably, and membrane formation nature falls that it is more than this.

[0009]

Tgn: Tg of the homopolymer of the presentation monomer n (absolute temperature)

Wn: weight fraction of the presentation monomer n [0010] Although the aquosity dispersing element of the polymer in this invention points out what the polymer is distributing into the dispersion medium which made aquosity media, such as water, the subject and it is prepared general conventionally by the well-known approach, for example, an approach given in JP,51-146589, A or JP,57-174301, A, obtaining by the usual emulsion-polymerization method is desirable. Manufacture by the emulsion-polymerization method can be performed to JP,55-110170,A etc. according to the approach of a publication. As a surfactant used when manufacturing according to an emulsion polymerization, cationic surface active agents, such as the fourth class salt of nonionic surface active agents, such as anionic surface active agents, such as the sulfate salt and sulfonate salt of the polyoxyalkylene alkyl aryl ether, and an alkyl allyl compound sulfonate, and polyoxyalkylene alkyl ether, or polyoxyethylene alkylammonium, an amphoteric surface active agent, etc. are mentioned, for example, 0.5 - 10% of the amount of the surface active agent to be used is suitable to the radical polymerization nature monomer whole quantity at a weight ratio, and is 1 - 6% preferably. Moreover, although the initiator used for the usual emulsion polymerization as a polymerization initiator can be used, the redox system which combined oxidizer independence or the oxidizer, and the reducing agent is desirable. For example, combination with reducing agents, such as peroxide independence, such as a hydrogen peroxide, persulfate, percarbonate, and a perboric acid salt, a water-soluble azo system initiator, these and sulfites, and sulfoxylate, is mentioned.

[0011] 0.1 - 5% of the amount of the polymerization initiator to be used is suitable to the radical polymerization nature monomer whole quantity at a weight ratio, and is 0.2 - 3% preferably. A polymerization initiator may be collectively added to the beginning of a reaction, and can also adopt the approach of adding continuously. Although reaction temperature is usually performed at 40-90 degrees C, it can also be carried out by less than [it] or more than it depending on the case. Thus, although about tens of millions to 1 billion high molecular weight may be shown if the polymer which has the specific monomer presentation ratio of above-mentioned monomer (1) - (4) generally has average molecular weight in hundreds of thousands or more and what has a high degree of cross linking, the aquosity dispersing element which hundreds of thousands - tens of millions of polymers distributed 40 to 60% of the weight preferably 30 to 70% of the weight in the aquosity medium is obtained. Here, aquosity solvents, such as ethanol, may be added to an aquosity medium, and a moisture content may be adjusted to it by the well-known approach after adjusting an aquosity dispersing element the abovementioned approach. The aquosity polish constituent of this invention can make the above-mentioned aquosity dispersing element an active principle, and can add and prepare kinds, such as the common component added by aquosity polish at this, for example, a wax, alkali fusibility resin, a plasticizer, or a polyvalent metal metal complex, or two sorts or more of mixture. Here, although the content in the aquosity polish constituent of the above-mentioned polymer is arbitrary, it is usually good to consider as 47 - 85 % of the weight preferably 38 to 91% of the weight.

[0012] Much more gloss, endurance, abrasion resistance, etc. are given to an aquosity polish constituent, a natural wax (for example, the Quan Delia wax, a KARUNABA wax, a dense wax), a synthetic wax (for example, polyethylene, polypropylene), and partial composition ester (for example, montan wax

derivative) are mentioned, and the polyethylene of a synthetic wax etc. is suitable for the wax which can be added to the aquosity polish constituent of this invention especially. The amount of the wax added is 5 - 35% preferably 5 to 50% to the resin solid content of an aquosity dispersing element. Moreover, the alkali fusibility resin which can be added to the aquosity polish constituent of this invention gives leveling nature to polish, and the resin which dissolves with alkali water solutions, such as caustic alkali of sodium and ammonia, is pointed out, for example, the condensation product of alpha and betaethylene nature partial saturation acid or an acid anhydride, the copolymer of styrene, an alkali fusibility alkyd resin, rosin and rosin, and polyhydric alcohol, MANIRAGAMU, a shellac, casein, Tell Ben resin, etc. are mentioned. They are an acid anhydride, the copolymer of styrene, the denaturation article of rosin ester, and an alkyl fusibility alkyd resin preferably. The amount of the alkali fusibility resin added is 2 - 20% preferably 0 to 40% to the resin solid content of an aquosity dispersing element. [0013] the plasticizer which can be added to the aquosity polish constituent of this invention can give film-forming and leveling nature to polish, and a coat degree of hardness can be adjusted -- solvents, such as a semipermanent or temporary plasticizer (film formation assistant), are pointed out. As a plasticizer, for example, dimethyl phthalate of a phthalic ester system, diethyl phthalate. The trimethyl phosphate of phosphoric ester systems, such as dibutyl phthalate and dioctyl phthalate, Triethyl phosphate, tributyl phosphate, tributoxyethyl phosphate, etc. are useful. As a film formation assistant, for example, the carbitols like ethyl carbitol and butyl carbitol The cellosolve acetates like the cellosolves like ethylcellosolve, butyl cellosolve, and iso-propyl cellosolve, ethylcellosolve acetate, and butyl-cellosolve acetate are useful. The above-mentioned plasticizer has 10 - 60% of preferably practical addition 5 to 75% to emulsion resin solid content. At 5% or less, a continuation coat is not formed for the addition of a plasticizer, but if 60% is exceeded, black heel-proof mark nature, blocking nature, and drying will fall. The class and the amount of this plasticizer used can take into consideration the effectiveness and compatibility of a coat formation temperature fall, and they can choose them suitably. [0014] The polyvalent metal complex which can be added to the aquosity polish constituent of this invention gives much more endurance and removal nature to polish, and dissolves polyvalent metal or its oxide, and salts in acids, such as carbonic acid, a formic acid, glutamic acid, and oxalic acid, for example, adjusts the water solution of these acids and salts of polyvalent metal to pH 7-11 by ammonia, an amine, etc. The thing using metals, such as zinc, beryllium, cadmium, copper, calcium, magnesium, a zirconium, barium, strontium, aluminum, a bismuth, antimony, lead, cobalt, iron, and nickel, as a polyvalent metal complex is mentioned, the carboxyl group by which the amount of the polyvalent metal complex added is contained in emulsion resin -- receiving -- 5 - 100% equivalence -- it is 10 -75% equivalence preferably. Various additives can be added to the aquosity polish constituent of this invention if needed in addition to the various above-mentioned components. For example, the fluorochemical surfactant of the fluoro alkyl group content which gives the leveling nature which was extremely excellent in the polish of this invention, a defoaming agent, a germicide, perfume, an antistatic agent, a slipping agent-proof, etc. are mentioned. 10 - 45% of desiccation solid content of the aquosity polish constituent by this invention is desirable, and it is 15 - 35% more preferably. [0015]

[Effect of the Invention] Aquosity glazing of the aquosity dispersing element of this invention can be carried out, and it can be broadly used as active principles, such as protective coating agents, such as wood, furniture, a metal, and plastics, including a constituent and a floor finishing compound. It is the good polish of the balance which was very excellent in glossiness, heel-proof mark nature, a water resisting property, and removal nature at the same time the tough coat which has chemical resistance is obtained, when [ at which the aquosity dispersing element of this invention is especially made into an active principle ] aquosity glazing is carried out and a constituent is applied to a floor etc. Next, an example explains this invention.

[0016]

[Example]

The aquosity resin dispersing element which is a copolymer of a monomer shown in the primary example was compounded by the emulsion-polymerization method usually used well. Among an

example, the section and especially a percentage are weight criteria, unless it describes.

\*\* Polymerization nature monomer glycidyl methacrylate A 5.0 section methacrylic acid 10.0 section styrene A 33.0 section ethyl acrylate A 18.0 section methyl methacrylate 34.0 section \*\* emulsifier polyoxyethylene nonyl phenol ethereal sulfate sodium (eight-mol addition of EO(s)) 3.0 section \*\* ion exchange water 126.4 section \*\* polymerization initiator ammonium persulfate The 0.3 \*\*\*\*\*\*\*\* emulsion-polymerization objects A-1 were pH5.0, 45% (25 degrees C, 30rpm, B mold) of solid content, and a stable aquosity dispersing element of viscosity 150cP.

[0017] Based on the raw material shown in Table 1 like example 2 example 1, the aquosity dispersing element A-2 to A-10 was manufactured.

Glazing of the example 3 aquosity dispersing element A-1 to A-10 was blended and carried out at each component and predetermined rate which are shown in Table 2, and the constituent was prepared. In order for this invention to carry out glazing and to clarify the engine performance of a constituent, the performance test was performed about the class product of Table 2. A trial item and a test method are described below.

According to the creation condition Japan floor polish Semiconductor Equipment & Materials International specification (JFPA-02) of a test piece, it carried out as follows. Namely, it dried for 24 hours, after it applied and extended so that coverage might serve as 10\*\*2 ml/m2 with the gauze cut to 0.6g, using a non asbestos floor tile as flooring, drying 30 minutes or more, applying the 2nd time and applying the 3rd time similarly.

[0018] The following trials were performed according to glossiness Japan floor polish Semiconductor Equipment & Materials International specification (JFPA-10). That is, according to JISZ8741 (specular-gloss measuring method), the glossiness (%) of 60 degrees was measured using the test piece prepared by the above-mentioned approach.

The following trials were performed according to heel-proof mark nature Japan floor polish Semiconductor Equipment & Materials International specification (JFPA-11). That is, viewing estimated ten steps of adhesion degrees of the black heel mark adhering to the test piece when examining using a heel mark testing machine using the test piece (white) prepared by the above-mentioned approach. (Ten points -> it has not adhered at all)

The following trials were performed according to the waterproof Japan floor polish Semiconductor Equipment & Materials International specification (JFPA-13). That is, after having made 0.1ml under \*\* the test piece prepared by the above-mentioned approach, covering with the cover glass and putting for 1 hour, the waterdrop which remained was sucked up and viewing estimated the milkiness condition of the test piece of the 1 hour after. The display of this evaluation is as follows.

O: -- a coat -- change-less \*\*: -- a coat -- a little -- xwith milkiness: -- a coat -- clear -- milkiness [0019] Using the test piece prepared by the approach above-mentioned [chemical-resistant (alcohol resistance)], it was immersed in the ethanol water solution 80% for 1 hour, and viewing estimated the milkiness condition of the test piece after desiccation. The display of this evaluation is as follows.

O: -- a coat -- change-less \*\*: -- a coat -- a little -- xwith milkiness: -- the coat performed the following trials according to the dip coating of milkiness or dissolution removal nature Japan floor polish Semiconductor Equipment & Materials International specification (JFPA-15) completely. That is, the test piece prepared by the above-mentioned approach was dipped in the standard removal liquid kept at 20\*\*2 degrees C for 20 minutes, and the situation of the removal after fully rinsing and drying with a stream was judged. The display of this evaluation is as follows.

O: -- the case where a coat is removed completely -- fitness x: -- case where it is not removed completely Poor -- [0020]

[Table 2] Table 2------Book From \*\* 1 2 3 4 5 [Combination formula]

The class of emulsification copolymer A-1 A-2 A-3 A-4 A-5 amount (45% of solid content) 20.4 This left This left This left This left E-4B\*1 (40% of solid content) 3.8 This left This left

The class of emulsification copolymer A-6 A-7 A-8 A-9 A-10 amount (45% of solid content) 20.4 This left This left This left This left High-tech E-4B\*1 (40% of solid content) 3.8 This left This lef

[Translation done.]